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ADIABATIC COMPUTATION OF INTERNAL BLAST

FROM MAGNESIUM-CASED CHARGES IN AIR

by

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April 1979

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FOREWORD

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INTRODUCTION

Previous communications from this laboratory have reported results of calculations on the adiabatic flame temperatures and resulting pressures from the constant-volume combustions of organic fuels in air[1] and of magnesium in air.[2] The present study represents a continuation of the foregoing, considering the effects to be observed when magnesium and fuel together undergo adiabatic constant-volume combustion in air.

As was the case previously, the calculations have been carried out on a desk-top computer (WANG 720C). Magnesium and fuel are considered to be uniformly distributed in the air volume at 25°C, one atmosphere. The air is assumed to be 78 mole percent N_2, 21 mole percent O_2, and one mole percent Ar.

The fuels considered were mannitol hexanitrate (nitromannite), PETN, HMX, Composition B-3, TNT, ethylene oxide, and THDC (exo-tetrahydrodicyclopentadiene). Formulas and a few significant properties of the fuels are given in Table 1.

In all the following, the symbol C will represent the charge, or the mass of fuel per cubic meter of air, and M the mass of magnesium per cubic meter of air. Charge-to-mass (C/M) ratios of 10:1, 3:1, 1:1, 1:3, and 1:10 were examined, with total concentration, C + M, ranging from 0.02 kg/m^3 to 10 kg/m^3.

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[1] Naval Weapons Center. *Peak Overpressures for Internal Blast*, by G. F. Kinney, R. G. S. Sewell, and K. I. Graham. China Lake, Calif., NWC. (NWC TP 6089, publication UNCLASSIFIED.) (In press.)

[2] Naval Weapons Center. *Reactive Metals in Internal Explosions: The Combustion of Magnesium in Air*, by R. A. Reinhardt. China Lake, Calif., NWC, February 1978. (NWC TM 3429, publication UNCLASSIFIED.)

TABLE 1. Properties of the Fuels

Designation	Name and Chemical Formula	$\Delta U_{f,298}$ (kJ/mole)	Relative Oxygen Content[a]
MHN	Mannitol hexanitrate (nitromannite) $C_6H_8N_6O_{18}$	−608.96	1.80
PETN	Pentaerythritol tetranitrate $C_5H_8N_4O_{12}$	−489.8	1.33
HMX	sym-Cyclotetramethylenetetra-nitramine, $C_4H_8N_8O_8$	+77.4	1.00
Comp B-3	60% RDX[b], 40% TNT $C_{2.05}H_{2.51}N_{2.15}O_{2.67}$[c]	−0.82[c]	0.81
TNT	2,4,6-Trinitrotoluene $C_7H_5N_3O_6$	−57.25	0.63
Ethylene Oxide	Epoxyethane C_2H_4O	−47.29	0.25
THDC	exo-Tetrahydrodicyclopentadiene $C_{10}H_{16}$	−104.9	0.00

[a] Number of oxygen atoms/(number of carbon plus half the number of hydrogen atoms).

[b] sym-Trimethylenetrinitramine (cyclonite).

[c] For a nominal formula mass of 100 g/mole.

BASIS OF CALCULATIONS

From the First Law of Thermodynamics it follows that for an adiabatic, constant-volume non-flow process there must be no net change in U, the internal energy; or the internal energy of all the products at the adiabatic flame temperature, T, must equal that of the reactants at entering conditions. For each component in the mixture of products, using the ideal-gas assumption throughout, we may write:

$$U_T = U_{298} + \int_{298}^{T} C_V dT,$$

where C_V is the heat capacity at constant volume. For U_{298} the customary thermochemical convention may be chosen of using the internal energy of formation of 298 K. The latter is defined as the internal energy change for the synthesis of the substance considered from the elements in their stable states at the given temperature (298 K). Of the reactant materials all but the organic fuel are elements in the stable state at 298 K, and thus the initial internal energy is just equal to the internal energy of formation of the fuel, ΔU_f, at 298. Hence, the adiabatic-isochoric condition may be written:

$$\sum_i U_{i,T} = \Delta U_f$$

the index, i, applying to all the product species.

A temperature must be found for which this criterion is met and which may then be identified as the adiabatic flame temperature. The pressure in the system is then calculated from the ideal gas law:

$$P = RT/V \sum n_i$$

in which n_i is the mole number for the ith product component, considering only the gaseous products, V the total volume (one cubic meter) and R the universal gas constant. The overpressure is found by subtracting one bar.

As before,[2] thermochemical data are represented by a five-parameter expression:

$$U_T = A + BT + CT^2 + DT^3 + E \log T$$

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Table 2 gives the internal energy parameters for the products considered; data from the JANAF Tables[3] were used as the primary source.

In Appendix C is described the condensed storage of the parameters expressing equilibrium constant and internal energy as functions of temperature.

EQUILIBRIUM CONSIDERATIONS

The following species are considered present in the product mixture: solid or liquid MgO (depending on whether the temperature is above or below the melting point, 3050 K), perhaps solid carbon, and the thirteen gases CO, CO_2, H, OH, H_2O, MgO, O, NO, Ar, H_2, Mg, N_2, and O_2. Speaking generally, in order to solve for the fifteen mole numbers of these species, there must be fifteen independent relations. Of these, 6 are the atom balance conditions (see Appendix A) for the 6 elements represented, and, thus, 9 equilibrium relations are required. These may be considered to be the vapor pressures of MgO and the equilibrium constants of formation of CO, CO_2, H, OH, H_2O, MgO(g), O, and NO. The three-parameter equation used by Kinney, et al,[1] log K = A + B/(C + T), based on data from the JANAF Thermochemical Tables[3] has been used. In Table 3 are listed the values of the parameters A, B, and C which were used in the computation. The methods for determining these parameters was described previously.[2]

The computation, at an assumed temperature, T, is greatly simplified by making use of the chemical behavior of the system. The following outlines the method used. More detail is given in Appendix B.

The mole number of MgO is found from the vapor pressure of the solid (if below 3050 K, the melting point) or liquid at the temperature T; the atom balance at the conclusion of computation showed no case in which all the MgO present was vaporized. In the most general case, there are 6 gaseous species to consider first in the computation (the "major species" of Appendix B): H_2, H_2O, CO, CO_2, O_2, Mg. From an initial approximation of one of them, the remaining 5 may be found from an appropriate combination of atom balance and equilibrium relations. The resulting 5 simultaneous nonlinear equations lead to a cubic equation in one unknown which may be solved iteratively. The results of this calculation then permit computation of the "high-temperature species", H, O, OH, and NO. An adjusted atom-balance conditions leads to the next iteration.

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[3] National Bureau of Standards. *JANAF Thermochemical Tables*, by D. R. Stull and H. Prophet, Project Directors. Washington, D. C., 2nd Ed., June 1971.

TABLE 2. Internal Energies of Products of Combustion
of Magnesium plus Organic Fuel in Air

Expressed as a function of τ, the absolute temperature in kilo-kelvins (τ = T/1000); values given in joules/mole:

$$U_T = A + B\tau + C\tau^2 + D\tau^3 + E \ln \tau$$

Substance	A	B	C	D	E
CO	-125179	28870	433	-37.6	-4560
CO_2	-421544	56400	251	13.4	-10000
H	213050	12470	0	0	0
OH	33024	18623	2533	-192.8	-450
H_2O	-254588	29480	5084	-403.2	-4930
MgO(s)[a]	-621030	53360	474	117.8	-3380
MgO(l)[a]	-562034	60670	0	0	0
MgO(g)	-7635	28690	299	-3.5	0
NO	75341	31460	-118	9.6	-5560
O	245728	11700	111	8.8	0
Ar	-3718	12470	0	0	0
H_2	-3789	15900	2933	-184.2	870
Mg(g)	136547	15270	-2339	326.9	7980
N_2	-16128	31900	-199	15.9	-7220
O_2	-8976	24270	1671	-88.3	-770
C(s)	-17007	29350	-524	52.9	-6800

[a] Values for solid and liquid MgO have been slightly corrected from those in Reference 2.

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TABLE 3. Equilibrium Constants Involved in
Magnesium-Fuel-Air Interactions

Logarithms (base 10) of the equilibrium constant of the indicated
reactions expressed as a function of absolute temperature

$$\log_{10} K = A + B/(C+T)$$

Constant	Reaction	A	B	C
K_{CO}	$C(s) + \frac{1}{2}O_2 = CO$	4.069	7440	184
K_{CO_2}	$C(s) + O_2 = CO_2$	−0.099	21100	18
K_H	$\frac{1}{2}H_2 = H$	3.242	−12280	35
K_{OH}	$\frac{1}{2}H_2 = \frac{1}{2}O_2 = OH$	0.662	−1720	−122
K_{H_2O}	$H_2 + \frac{1}{2}O_2 = H_2O$	−3.100	13420	20
K_{MgO}	$Mg(g) + \frac{1}{2}O_2 = MgO(g)$	−1.772	7270	−181
K_{NO}	$\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$	0.645	−4650	−15
K_O	$\frac{1}{2}O_2 = O$	3.545	−13550	16
	$MgO(s) = MgO(g)$	8.239	−27570	−104
	$MgO(1) = MgO(g)$	6.65	−22500	−154

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Several special cases should be indicated:

Case I. Oxygen is in excess over both carbon (to CO) and magnesium.

Case II. Insufficient oxygen for both carbon and magnesium; no solid carbon present.

Case III. Solid carbon is present.

Case IV. At the extreme of high magnesium concentration, crystalline magnesium nitride will form, sometimes accompanied by condensed elemental magnesium metal (Table 4). Because of the memory limitations of the WANG calculator, it was not practicable to include this case in the computations. These points have thus been omitted (and are so indicated in Table 5).

RESULTS

In Table 5 are given the results of the computations. The table is in five sections, corresponding to the five values of the charge-to-mass ratio (C/M) chosen. For each point the upper figure is the over-pressure (P - 1, in bars) and the lower, in parentheses, is the Kelvin temperature. Moving down any column of this table corresponds to increasing the total concentration, C + M, for a fuel-magnesium mixture of fixed C/M. Typically, the temperature reaches a maximum about where the system is just balanced in oxygen for the formation of CO + H_2O. For example, for TNT at C/M = 1.0, the temperature maximum occurs at C = 0.5 kg/m^3, M = 0.5 kg/m^3. Beyond here, it is to be noted that the pressure continues to rise even as the temperature falls as a result of increasing quantity of gaseous products. At the last point (C and M each 5 kg/m^3) the temperature is a bit higher than the preceding; this is always observed when the smoke point is reached (when solid carbon forms). The carbon is formed chiefly from the reaction CO(g) = C(s) + MgO(s), a highly exothermic reaction.

The points indicated by note a in Table 5 are those for which Mg_3N_2 is produced. As pointed out earlier, it was not practicable to program for this case; it can be said, nonetheless, that the pressures will be very much smaller than otherwise because of the consumption of four moles of gas per mole of Mg_3N_2 formed.

Table 6 gives product yields (as mole-fraction in the gas) for this series just referred to: TNT at C/M = 1.0. The extreme complexity found at the middle concentrations—say, from C + M = 0.20 to 1.0 kg/m^3— should be noted: each of the thirteen gaseous species is present in appreciable quantity. Such data, though not included in this report, are available for all the other points computed.

Figures 1 and 2 show the pronounced effect of total concentration (C + M) on overpressure; the cases chosen for Figure 1 are for HMX at three charge-to-mass ratios. About the same appearance is to be observed with any of the other explosive fuels. The hydrocarbon, THDC,

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TABLE 4.   Logarithm (base 10) of the Dissociation
Constant for Magnesium Nitride

$$K_p = P_{Mg}^3 P_{N_2}$$

T, K	$Log_{10} K_p$
900	−19.56
1000	−16.21
1100	−11.10
1200	−9.16
1300	−7.52
1400	−5.89
1500	−3.71
1600	−1.82
1700	−0.15
1800	1.33
1900	2.65
2000	3.84
2100	4.90
2200	5.87
2300	6.75

TABLE 5. Overpressure (bars) and Temperature (in parentheses)
for the Adiabatic, Constant-Volume Combustion of Fuels
Plus Magnesium in Air.

C/M	Fuel	Mg	NM	PETN	HMX	B-3	TNT	C_2H_4O	THDC
1:1	.01	.01	1.16 (638)	1.22 (659)	1.26 (671)	1.34 (695)	1.46 (732)	1.92 (866)	2.39 (1006)
	.02	.02	2.19 (945)	2.29 (977)	2.39 (998)	2.51 (1040)	2.71 (1103)	3.49 (1329)	4.28 (1566)
	.05	.05	4.7 (1670)	4.9 (1732)	5.0 (1774)	5.3 (1856)	5.7 (1980)	7.1 (2369)	8.3 (2700)
	.1	.1	7.7 (2526)	8.0 (2601)	8.3 (2657)	8.5 (2752)	8.9 (2869)	10.1 (3050)	10.7 (3034)
	.2	.2	10.4 (3107)	10.7 (3147)	11.0 (3193)	11.2 (3234)	11.5 (3276)	12.9 (3149)	10.3 (2183)
	.5	.5	16.2 (3574)	16.8 (3559)	17.7 (3550)	17.8 (3503)	17.9 (3371)	16.5 (2297)	13.7 (2201)
	1	1	25.4 (3766)	26.5 (3699)	28.2 (3618)	28.0 (3457)	27.0 (3050)	25.1 (2363)	18.2 (2010)
	2	2	44.0 (3922)	46.1 (3802)	49.1 (3636)	47.2 (3284)	39.2 (2501)	42.4 (2441)	a
	5	5	101.1 (4138)	105.9 (3948)	112.1 (3652)	103.2 (3050)	87.7 (2655)	95.3 (2566)	a
1:3	.005	.015	1.47 (735)	1.51 (750)	1.53 (756)	1.56 (767)	1.61 (785)	1.85 (852)	2.09 (923)
	.01	.03	2.72 (1118)	2.77 (1133)	2.81 (1143)	2.87 (1163)	2.97 (1194)	3.35 (1306)	3.75 (1428)
	.02	.06	4.8 (1742)	4.8 (1767)	4.9 (1784)	5.0 (1818)	5.2 (1870)	5.8 (2046)	6.4 (2236)

TABLE 5. (Cont'd)

C/M	Fuel	Mg	NM	PETN	HMX	B-3	TNT	C_2H_4O	THDC
1:3	.05	.15	8.6 (2949)	8.7 (2967)	8.8 (2988)	8.9 (3016)	9.0 (3050)	9.2 (3050)	9.7 (3128)
	.1	.3	10.6 (3378)	10.7 (3382)	10.9 (3394)	11.0 (3402)	11.1 (3411)	12.0 (3364)	12.0 (3109)
	.2	.6	14.3 (3613)	14.5 (3588)	14.9 (3568)	15.0 (3538)	15.1 (3482)	15.8 (3132)	12.7 (2260)
	.5	1.5	25.2 (3648)	25.5 (3557)	26.0 (3440)	25.4 (3261)	25.3 (3050)	22.5 (2363)	19.0 (2194)
	1	3	43.0 (3588)	42.8 (3398)	41.8 (3087)	41.3 (2885)	35.4 (2461)	36.8 (2408)	a
	2	6	77.7 (3485)	74.4 (3138)	76.2 (2931)	66.7 (2551)	63.2 (2543)	65.3 (2439)	a
1:10	.002	.02	1.79 (848)	1.83 (851)	1.84 (854)	1.85 (858)	1.87 (865)	1.96 (891)	2.06 (919)
	.004	.04	3.29 (1301)	3.31 (1306)	3.32 (1310)	3.35 (1318)	3.38 (1330)	3.50 (1374)	3.69 (1422)
	.01	.1	6.6 (2352)	6.6 (2361)	6.6 (2369)	6.7 (2382)	6.7 (2405)	7.0 (2473)	7.2 (2552)
	.02	.2	8.6 (3075)	8.5 (3077)	8.7 (3087)	8.7 (3097)	8.8 (3112)	9.0 (3144)	9.2 (3184)
	.04	.4	11.0 (3514)	11.0 (3510)	11.6 (3521)	11.1 (3510)	11.2 (3509)	11.5 (3479)	11.8 (3424)
	.1	1	17.0 (3543)	17.0 (3515)	17.2 (3486)	17.1 (3454)	17.1 (3404)	17.2 (3183)	16.5 (2740)

TABLE 5. (Cont'd)

C/M	Fuel	Mg	NM	PETN	HMX	B-3	TNT	C_2H_4O	THDC
	.2	2	25.3 (3201)	24.9 (3100)	25.2 (3050)	25.7 (3050)	25.1 (2906)	21.8 (2335)	20.2 (2244)
	.4	4	39.9 (2729)	37.4 (2500)	35.4 (2336)	34.8 (2327)	34.1 (2318)	33.3 (2179)	a
3:1	.015	.005	0.79 (530)	0.90 (561)	0.98 (580)	1.10 (620)	1.28 (675)	1.98 (880)	2.68 (1087)
	.03	.01	1.60 (761)	1.78 (813)	1.87 (846)	2.11 (912)	2.44 (1010)	3.63 (1351)	4.79 (1699)
	.06	.02	2.96 (1139)	3.26 (1225)	3.47 (1282)	3.84 (1394)	4.38 (1560)	6.3 (2100)	8.0 (2568)
	.15	.05	6.2 (1978)	6.8 (2128)	7.2 (2230)	7.8 (2419)	8.6 (2656)	10.7 (2977)	9.9 (2527)
	.3	.1	10.1 (2766)	10.7 (2885)	11.3 (2973)	11.5 (3050)	11.8 (3113)	13.5 (2897)	9.9 (2055)
	.6	.2	14.3 (3170)	15.2 (3233)	16.1 (3302)	16.4 (3324)	16.6 (3266)	15.6 (2217)	12.0 (2033)
	1.5	.5	26.1 (3547)	27.8 (3553)	30.2 (3562)	30.2 (3451)	28.8 (3050)	27.3 (2299)	17.5 (1803)
	3	1	45.4 (3762)	48.8 (3733)	53.5 (3690)	52.6 (3468)	42.3 (2481)	47.0 (2376)	a
	6	2	84.6 (3962)	91.2 (3904)	100.7 (3817)	97.4 (3474)	77.9 (2597)	87.0 (2466)	a

TABLE 5.   (Cont'd)

C/M	Fuel	Mg	NM	PETN	HMX	B-3	TNT	C_2H_4O	THDC
10:1	.02	.002	0.61 (473)	0.76 (516)	0.85 (544)	1.03 (598)	1.29 (676)	1.72 (941)	3.11 (1208)
	.04	.004	1.30 (667)	1.55 (739)	1.71 (784)	2.02 (874)	2.45 (1006)	4.02 (1451)	5.52 (1893)
	.10	.01	3.01 (1114)	3.51 (1253)	3.87 (1344)	4.46 (0522)	5.3 (1782)	8.2 (2514)	9.2 (2713)
	.2	.02	5.4 (1667)	6.2 (1881)	6.9 (2024)	7.8 (2228)	8.9 (2611)	11.1 (2873)	8.2 (1894)
	.4	.04	9.3 (2379)	10.4 (2615)	11.3 (2763)	12.0 (2939)	12.6 (3050)	13.0 (2470)	7.8 (1507)
	1	.1	17.3 (3050)	18.5 (3135)	20.1 (3234)	20.5 (3250)	20.0 (3067)	17.8 (2002)	9.4 (1226)
	2	.2	28.3 (3291)	30.7 (3363)	33.8 (3428)	33.7 (3331)	31.2 (2917)	27.6 (1945)	12.3 (1116)[b]
	4	.4	50.5 (3494)	55.6 (3538)	61.2 (3571)	59.8 (3374)	47.3 (2434)	47.2 (1906)	c
	10	1	118.3 (3716)	129.7 (3738)	144.6 (3742)	138.8 (3440)	109.0 (2578)	106.4 (1884)	a

[a] Mg_3N_2 is found in these cases.

[b] 1.8 kg/m^3 of fuel, 0.18 k/m^3 of air.

[c] Failed to converge.

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TABLE 6. Product Yield for TNT-Mg, C/M = 1.0

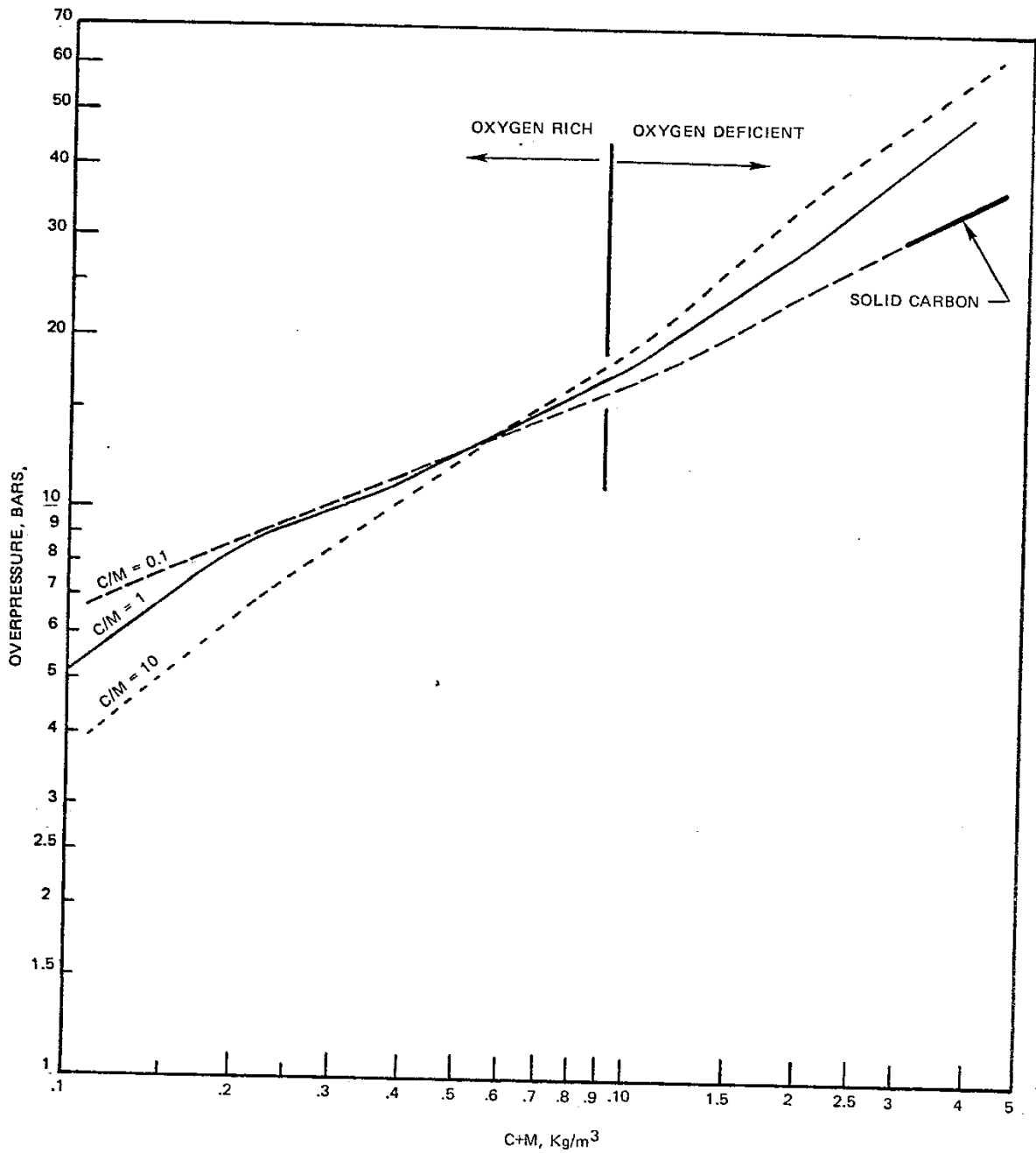| C + M →	0.02	0.04	0.10	0.20	0.40	1.0	2.0	4.0	10.0
CO	0	0	.0042	1.31	8.07	21.7	27.8	29.4	28.0
CO_2	.763	1.52	3.79	6.12	5.39	1.20	.129	.0013	.0018
H_2	0	0	.0003	.0658	.596	4.80	9.14	11.3	13.6
H_2O	.272	.544	1.34	2.13	3.05	2.07	.308	.0032	.0056
O_2	19.9	18.8	15.2	8.75	2.43	.0193	0	0	0
Mg(g)	0	0	0	.0239	1.09	12.7	26.4	35.8	42.1
MgO(g)	0	0	0	.189	2.26	2.44	.275	.0014	.0031
N_2	78.1	78.1	78.0	76.2	70.6	51.6	34.5	23.1	16.1
Ar	.999	.998	.994	.973	.881	.600	.366	.209	.100
H	0	0	.0001	.0846	.752	2.20	1.05	.134	.187
O	0	0	.0087	.667	1.19	.113	0	0	0
OH	0	0	.0385	.824	1.57	.413	.0123	0	0
NO	.0001	.0090	.654	2.68	2.17	.181	.0026	0	0
C(s) ?	—	—	—	—	—	—	—	—	+
ΔP, bars	1.46	2.71	5.68	8.89	11.47	17.86	27.0	39.2	87.7
T, K	732	1103	1980	2869	3276	3371	3050	2501	2655

Mole percent

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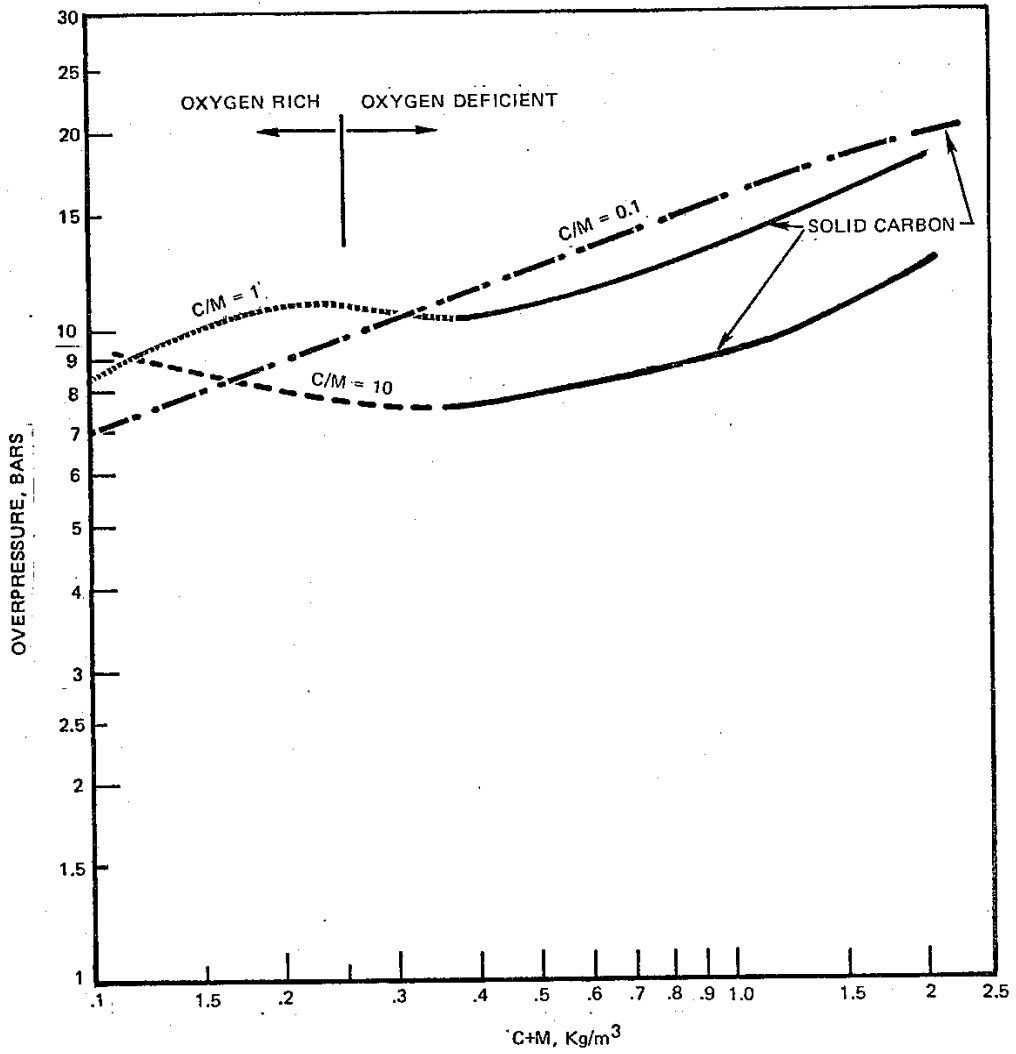FIGURE 1. HMX; Overpressure vs Total Concentration

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FIGURE 2. THDC: Overpressure vs Total Concentration

shows quite a different behavior (Fig. 2), with ethylene oxide rather intermediate between these examples. The decreases in pressure seen for THDC are real and are a result of the early exhaustion of the oxygen supply.

Figures 3 and 4 illustrate the rather small effects of charge-to-mass ratio on the overpressure. Figure 3, for Comp. B-3, is typical of the oxygenated materials, with decreasing pressure at low total concentration and increasing at high. The opposite effect is seen in Figure 4, for THDC. At low concentrations (small values of C + M) the systems are oxygen-rich, virtually complete combustion occurring in all cases. The heating value (ΔU of combustion) per unit mass is about 50% greater for a hydrocarbon than for magnesium (due to the lower atomic mass of carbon); hence increasing C/M (i.e., replacing magnesium by fuel) results in increased temperature, and thus pressure, with the hydrocarbon. But with the explosive fuels, the heating value is less than magnesium per unit mass (a result of the nitrogen and oxygen content) so that a decrease is seen in this same region. For ethylene oxide, which has about the same heating value as magnesium, there is very little effect of C/M on overpressure at low concentrations.

At high concentrations the systems are all oxygen-deficient. Replacing magnesium by hydrocarbon (THDC) serves to exacerbate the oxygen deficiency, whereas the oxygen content of any of the explosive fuels chosen will improve the oxygen balance and thus increase the pressure.

In Figure 5 is shown the effect of the different fuels, all at C/M = 1.0 and for a variety of total concentrations. The ordinate of this plot is a "relative oxygen content," computed for each pure fuel as the number of oxygen atoms divided by the sum of the number of carbon atoms plus half the number of hydrogen atoms. For the most part, there are no profound effects to be seen; there is, however, a broad maximum in pressure at HMX, which is fuel just oxygen-balanced to CO plus H_2O. At the higher concentrations, ethylene oxide shows a larger overpressure than might be expected. This is a result of its high hydrogen content, leading at these conditions to a large partial pressure of hydrogen gas.
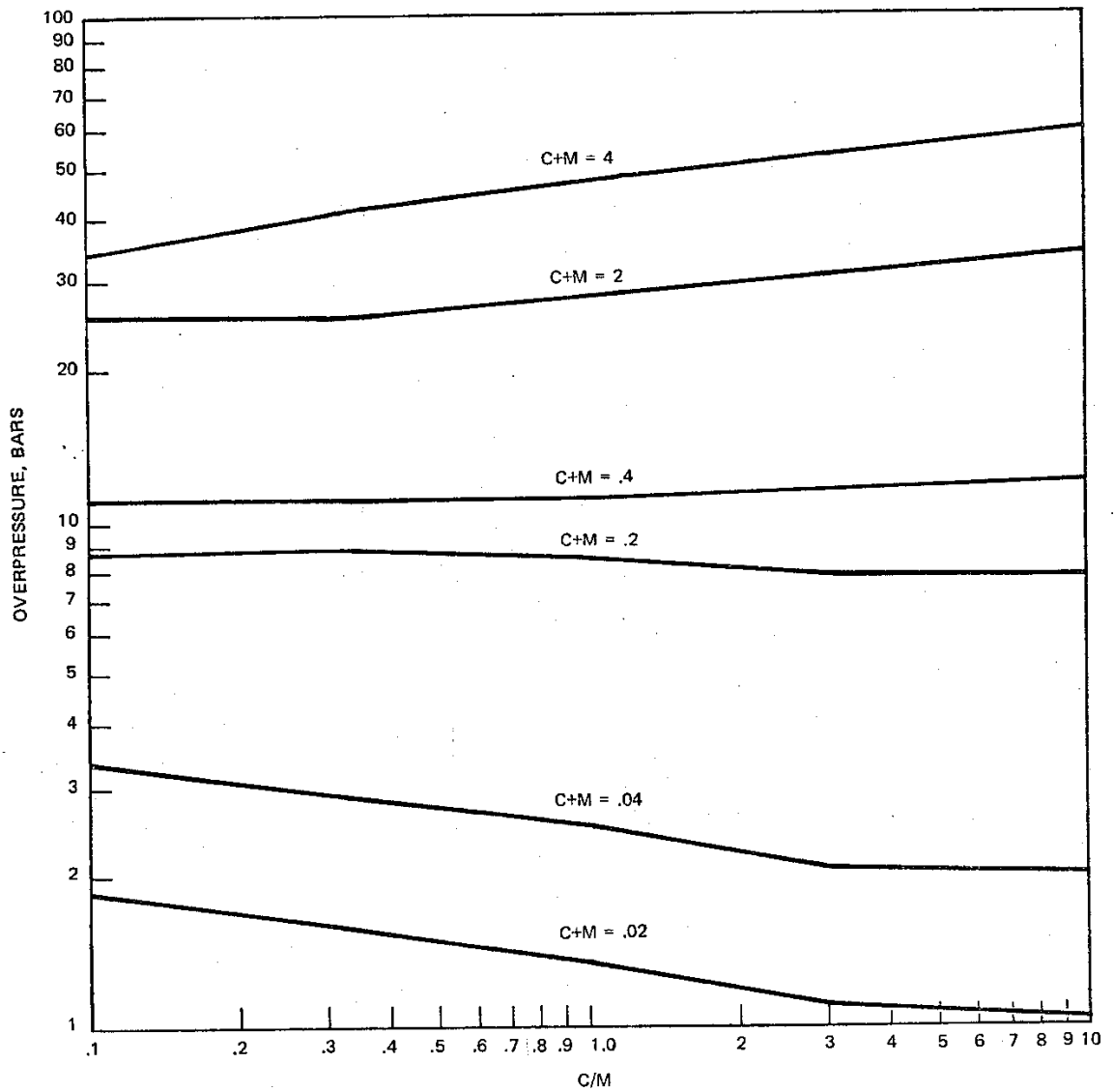
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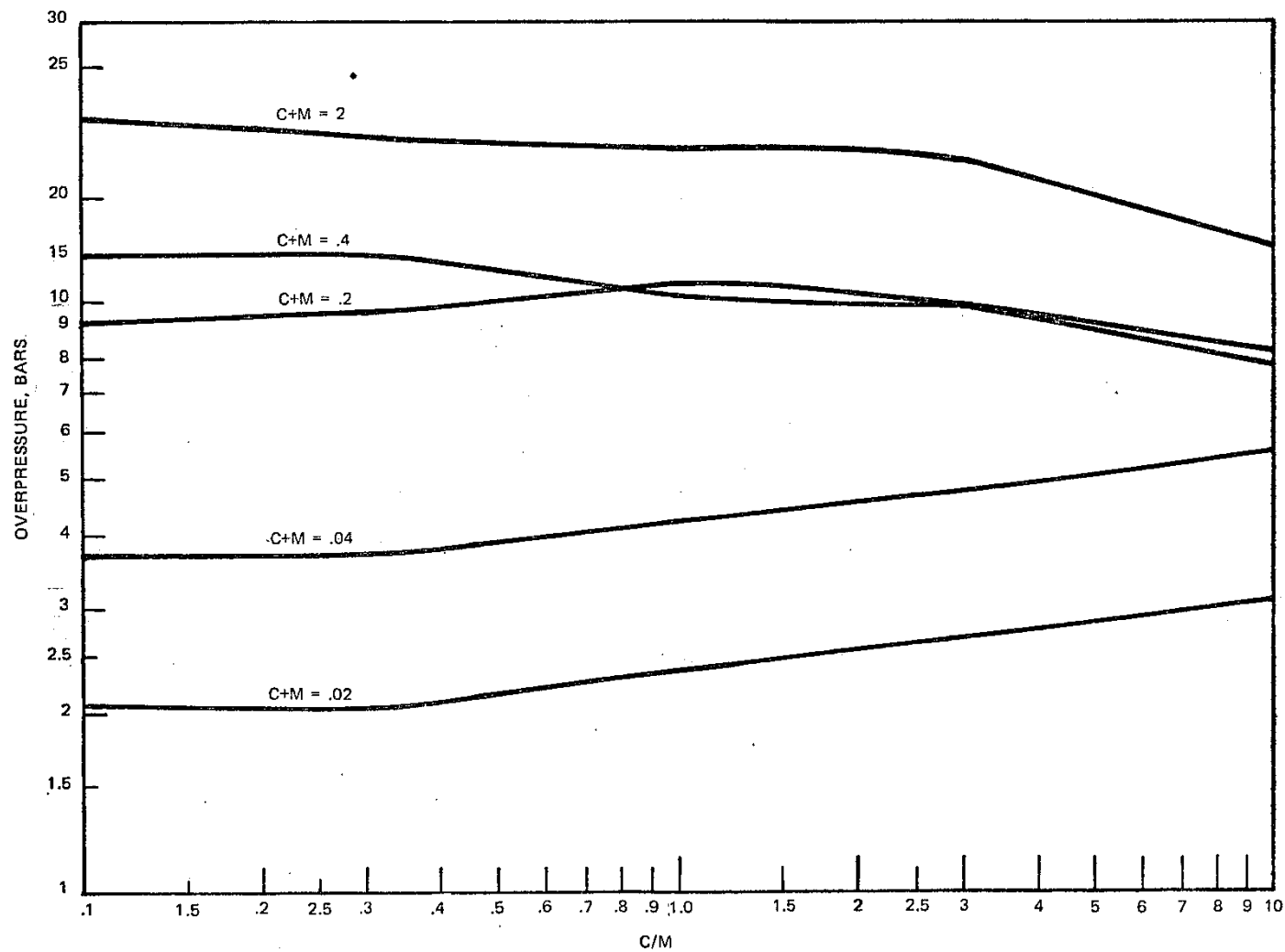FIGURE 3. Comp. B-3; Overpressure vs Charge-to-Mass Ratio at Various Total Concentrations (in Kg/m^3).

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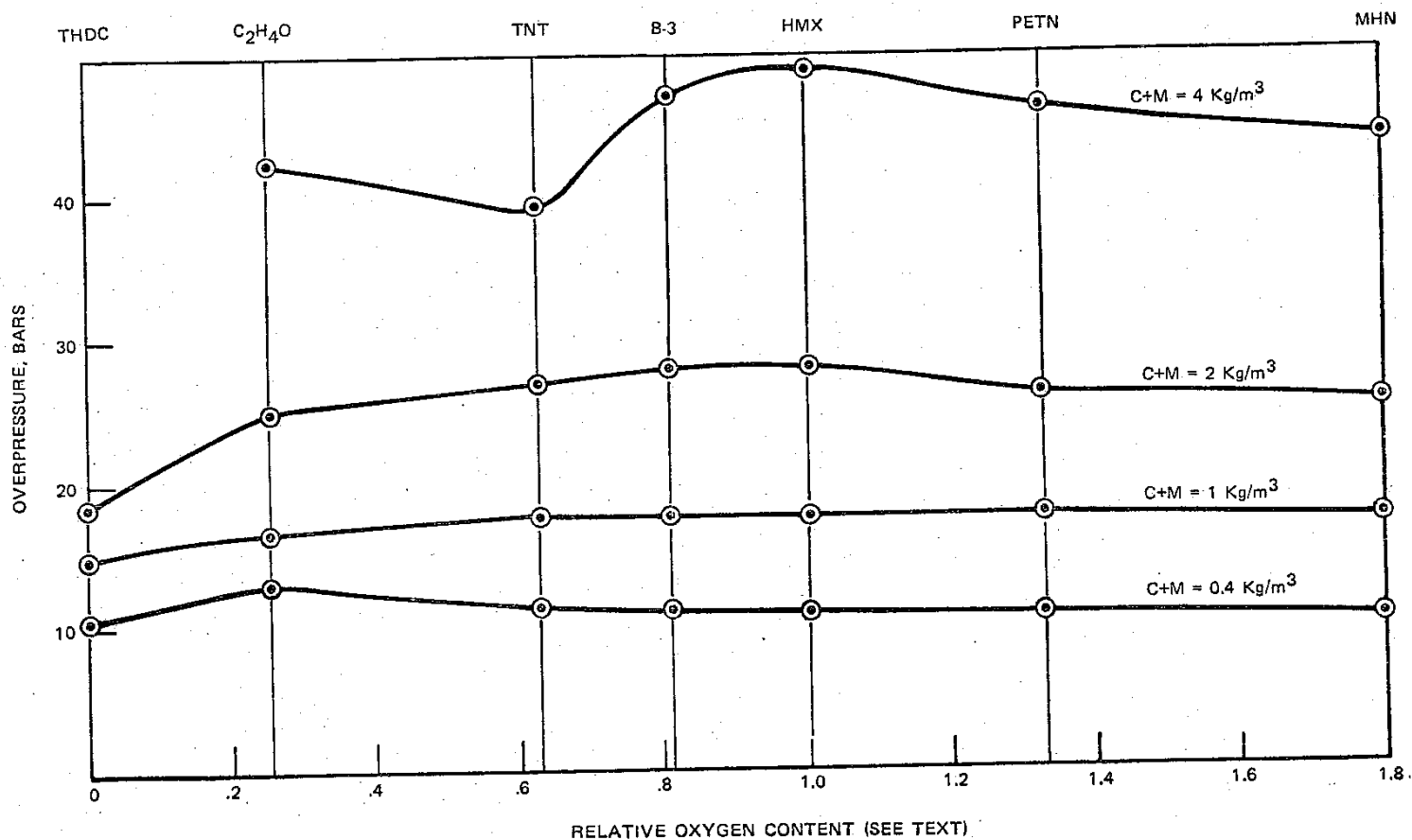FIGURE 4. THDC: Overpressure vs Charge-to-Mass Ratio at Various Total Concentrations (in Kg/m^3)

FIGURE 5. Effect of Fuel on Overpressure for C/M = 1.0

Appendix A

EQUILIBRIUM AND ATOM-BALANCE RELATIONS

The thermodynamic equilibrium constant for a reaction involving
gases is expressed in terms of the partial pressures (for ideal gases;
fugacities in general) of the reactant and product species. This is
to say that the standard state for the gas is at unit pressure (fugac-
ity). Such equilibrium constants, denoted K_p, are those usually found
tabulated in the literature.

For calculations in constant-volume systems, however, it is more
convenient to use the equilibrium constant expressed in mole numbers,
K_n. Writing a chemical equation as

$$\sum_i \nu_i A_i = 0$$

where A_i are the formulas of the chemical species as ν_i the stoichio-
metric coefficients, negative for reactants and positive for products,

$$K_p = \prod_i p_i^{\nu_i} \quad \text{(assuming all substances are ideal gases)},$$

$$K_n = \prod_i n_i^{\nu_i} \quad \text{and it follows from the ideal gas law}$$
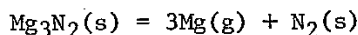
that

$$K_n = K_p \left[\frac{V}{RT}\right]^{\Delta\nu}$$

where $\Delta\nu$ is the change in the number of moles of gas. The inclusion of
pure condensed phases causes no complication; each, when present, is in
its standard state (unit activity) and it is omitted from the equili-
brium expression and, likewise, not counted in the evaluation of $\Delta\nu$.

The data of Table 3 yields K_p values (taken from References 1 and
2). Save for the vapor pressure[3] of condensed MgO (the last two given)

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these are all equilibrium constants of formation; i.e., for the synthesis of one mole of the indicated substance from the elements in their reference states: $H_2(g)$, graphite, $O_2(g)$, $N_2(g)$, $Mg(g)$. The selection of magnesium vapor as the reference state for magnesium, even at temperatures below the normal boiling temperature, 1378 K, was made for reasons of convenience in fitting the data and leads to no inconsistencies in results.

Table 4 lists values for the $\log_{10} K_p$ of the dissociation of $Mg_3N_2(s)$ into gaseous elements:

$$Mg_3N_2(s) = 3Mg(g) + N_2(s)$$

that is,

$$K_p = p_{Mg}^3 p_{N_2}$$

Data above 1300 K are taken directly from Reference 3; those below that temperature include also the vapor pressure of solid or liquid magnesium from the same source.

Formulas enclosed in brackets represent mole numbers; the symbol a_X represents the number of moles of atoms of element X in the system. The six atom balance equations are:

$$[Ar] = 0.4036$$
$$[CO] + [CO_2] = [C(s)] = a_C$$
$$[H] + [OH] + 2[H_2O] + 2[H_2] = a_H$$
$$[NO] + [N_2] = a_N$$
$$[OH] + [H_2O] + \sum MgO + [NO] + [O] + 2[O_2] = a_O$$
$$[Mg] + \sum MgO = a_{Mg},$$

where $\sum MgO = [MgO(s \text{ or } l)] + [MgO(g)]$.

In actual practice the oxygen and magnesium balances are often combined:

$$a_O - a_{Mg} [OH] + [H_2O] + [NO] + [O] + 2[O_2] - [Mg]$$

thus eliminating the need to compute the mole numbers of condensed MgO. Moreover, in the computational routines, what we may refer to as "adjusted" stoichiometric conditions are used. For example,

$$[H_2O] + [H_2] = 1/2 \left(a_H - [H] - [OH] \right)$$

making use of previously computed or estimated values of [H] and [OH].
Similar "adjusted" oxygen-magnesium balance relations are used in a
variety of forms.

Appendix B

EQUILIBRIUM COMPUTATIONS

The following is an outline of the computational algorithm referred to in the body of this report in the section "Equilibrium Considerations". The notation is that described in Appendix A.

[Ar] is given by its value in air, 0.4036 moles/m^3 and [MgO(g)] is computed from the vapor pressure of the appropriate condensed phase. The mole numbers of the condensed phases themselves are computed after all other computations, making use of the atom balance equation:

$$[MgO(s \text{ or } l)] = a_{Mg} - [Mg] - [MgO(g)]$$

When present,

$$[C(s)] = a_C - [CO] - [CO_2]$$

In each iteration, after the principal computations have been done the "high-temperature species" H, OH, O, and NO are found from the appropriate equilibrium constants of formation (see Table 1). [N_2] is then adjusted for the loss of N atoms into NO.

There remain 6 gaseous species (referred to in the following as the "major" species) to consider: H_2, H_2O, CO, CO_2, O_2, Mg.

Case I: Oxygen is in excess over both C (to CO) and Mg; that is, $a_O - a_C - a_{Mg}$ is positive. [O_2]$_0$ is assumed equal to this excess; the present value of [O_2] is used to solve the pair of simultaneous equations involving carbon-atom balance (CO and CO_2 only, since solid carbon will not be present in this case) and the CO - CO_2 equilibrium expression:

$$[CO_2]/[CO][O_2]^{1/2} = K_{CO_2}/K_{CO}$$

In like manner [H_2] and [H_2O] are computed from the adjusted hydrogen balance (see Appendix A) and the formation equilibrium constant of H_2O. [Mg] is computed from the known [MgO] and the present approximation to [O_2]. Following computation of the high-temperature species, a new [O_2] is found from the atom balance in oxygen; this is averaged with the preceding value to compensate for overcorrection. Convergence is tested on an adjusted oxygen-balance condition.

Case II: Oxygen is insufficient for both carbon and magnesium; no solid carbon is present.

The initial $[O_2]$ is zero; successive approximations are generated at the end of each iteration. The remaining major species are solved through use of three atom-balance conditions: C, H (adjusted) and O (adjusted); and two equilibrium relations:

$$[CO_2][H_2]/([CO][H_2O]) = K_{CO_2}/(K_{CO}K_{H_2O})$$

and

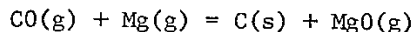$$[CO_2][Mg]/([CO][MgO]) = K_{CO_2}/(K_{CO}K_{MgO})$$

recalling that, in the last, [MgO] is a known quantity. These five simultaneous equations lead to a cubic equation in $[CO_2]$, which is solved by the Newton-Raphson approximation method. The correct root will lead to positive values, on back substitution into the system of simultaneous equations, for all mole numbers. $[O_2]$ is computed from [Mg] and the formation equilibrium constant of MgO. After checking an adjusted oxygen balance, this new $[O_2]$, averaged with the previous one, is used to initiate the next approximation.

After convergence, the presence or absence of solid carbon is checked by evaluating $[CO_2]/([O_2]K_{CO_2})$. If this is greater than unity, solid carbon is present and the logic switches to Case III below.

Case III: Solid carbon is present.

If $a_{Mg} - a_O$ is positive, this difference is used as the initial approximation for [Mg]. $[O_2]$ is computed from the known [MgO], K_{MgO} and the present approximation for [Mg]. From $[O_2]$ can be computed [CO] and $[CO_2]$, using the appropriate formation equilibrium constants, and also $[H_2O]$ and $[H_2]$ by including the adjusted hydrogen-atom balance. A new [Mg] is found from the combined magnesium-oxygen balance relation for the next iteration.

If $a_{Mg} - a_O$ is negative, it is necessary to consider the equilibrium

$$CO(g) + Mg(g) = C(s) + MgO(g)$$

that is,

$$[CO][Mg] = [MgO] K_{CO} K_{MgO}$$

and an adjusted oxygen-magnesium balance:

$$w = a_O - a_{Mg} - [OH] - [O] - [NO] - 2[O_2] - 2[CO_2] - [H_2O] = [CO] - [Mg]$$

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The solution to the quadratic equation resulting from this simultaneous pair yields [Mg], from which all the remaining mole numbers are computed as in the first statement in this case. A corrected value of w is used for the iteration.

At the conclusion of computation, a check was made for the possible formation of crystalline magnesium nitride. The product $p_{Mg}^3 p_{N_2}$ was computed; if the computed product is greater than the equilibrium value (Table 4) the indication is that Mg_3N_2 indeed forms and the previous results for that point are discarded

Appendix C

CONDENSED STORAGE OF INTERNAL-ENERGY AND
EQUILIBRIUM-CONSTANT PARAMETERS

Memory space in the WANG computer is severely limited for a pro-
gram of this complexity: there are 248 memory registers available for
storage of data or program, each two program steps requiring 16 memory
registers. To help overcome this limitation a condensed form of stor-
age for the thermochemical-thermodynamic parameters was used. Thus,
two registers were used to store the five internal-energy parameters
of Table 2 (with sign) for each substance; and a single register per
substance sufficed for the three equilibrium parameters of Table 3. To
give one example only, the constants A and C of the internal-energy
equation ($U_T = A + B\tau + C\tau^2 + D\tau^3 + E \ln \tau$) are stored in the form
a.c., where a = A (the sign of A being given by the sign of the stored
number) and $0.c = 10^{-5}(C + 10^4)$, allowing thus for negative as well as
positive values of C. The only limitation to this method lies in the
number of significant digits: for the entire contents of the storage
register twelve digits are stored, not counting sign, decimal point,
or power of ten.